

UDC 666.1.031.13:66.046.512:66.040.262.2

CHANGE IN THE REDOX POTENTIAL OF A GLASS MELT UPON INTRODUCING A MELTING CATALYST INTO THE GLASS BATCH

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Translated from *Steklo i Keramika*, No. 3, pp. 5–7, March, 2000.

The change in the direction of the redox equilibrium $\text{Fe(II)} = \text{Fe(III)}$ and $\text{S(IV)} = \text{S(VI)}$ in glass melting upon introducing sodium silicofluoride as a melting catalyst is considered.

Practical experience indicates that the efficiency of glass melting for clear silicate glass depends largely on its content of bivalent and trivalent iron oxides, which exist in the melt in the state of the redox equilibrium



The ratio between the oxidized Fe(III) and reduced Fe(II) forms of iron oxides can vary within a wide range in conformance with the redox potential (ROP) of the glass melt, which depends on a number of factors. These factors include the chemical composition of the glass, the time and temperature parameters of the process, the composition of the gas medium, and the ROP of the glass batch [1]. An increased content of iron oxide in its reduced form Fe(II) has a negative effect on glass melting [2], due to decreased diathermancy of the melt. The latter factor degrades the conditions for penetration of IR radiation into the glass-melt depth, causes delays in the glass-melting stages, and decreases the melt homogeneity.

In the traditional technology for making clear sheet glass, a specified diathermancy level is ensured by maintenance of constant temperature and gas conditions of the melting process and joint introduction of oxidizers (sodium sulfate) and reducers (anthracite) into the batch in strictly specified quantities.

In some cases, melting catalysts are introduced into the batch in order to intensify the melting process. The most common melting accelerator until the mid-eighties was sodium silicofluoride. This component is currently used in the production of photochromic glasses, light filters [3, 4], etc., taking into account environmental-safety requirements. Recommendations for using this agent in glass melting are given in [5].

However, in spite of the wide application of this material in glass engineering, there is still no unified opinion as to its

accelerating effect on various stages of glass melting. On the one hand, it was noted [1] that fluorides significantly improve the conditions of batch melting and clarification, due to formation of a low-temperature eutectic at 550–600°C. On the other hand, fluorides contain both alkaline (Na^+) and acid (F^-) ions, and therefore, introduction of fluorides can significantly modify the glass-melt ROP and the ratio between the reduced and oxidized forms of iron. The latter aspect has hardly been investigated in the technical literature and undeniably merits more detailed study.

Let us seek to interpret the effect of the melting catalyst Na_2SiF_6 on the glass-melt ROP by studying the change in the iron redox equilibrium in the industrial process of production of sheet glass for construction.

The technological process was studied in a regenerative glass-melter with a laterally directed flame heated by natural gas. The daily output of the furnace was 140 tons of liquid glass. The design parameters of the furnace and the basic parameters of glass melting and glass-band formation are given in [6].

It should be noted that direct measurement of the glass-melt ROP is a technically difficult problem that is beyond the scope of the present study. Since iron oxides in silicate melts always exist in the state of the redox equilibrium (1), the following glass basicity index [6] was used for the purpose of the present study:

$$d_{\text{Fe(II)}} = \text{Fe(II)} \times 100 / (\text{Fe(II)} + \text{Fe(III)}),$$

where Fe(II) and Fe(III) are the absolute weight content of the bivalent and trivalent ferric oxides, converted to the metal.

This index represents the relative fraction in iron of the lower valence $d_{\text{Fe(II)}}$ and allows indirect characterization of the ROP of the glass melt in the course of melting. The method for determining the content of Fe(II) and Fe(III) is simple and was described in [6].

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TABLE 1

Technological process	Chemical composition of glass (from analysis), wt. %				Glass melt temperature, °C		Batch ROP	Integral light transmission of glass 1 cm thick, %	Weight content, %		Weight content of Na ₂ SiF ₆ in batch, %
	SiO ₂ + Al ₂ O ₃	MeO + Me ₂ O	Fe ₂ O ₃	SO ₃	in clarification (lg η = 2)	in glass band formation (lg η = 3)			Fe(II)	d _{Fe(II)}	
Before introducing Na ₂ SiF ₆	73.50	25.90	0.057	0.50	1520	1170	15.06	86.7	0.017	37.9	0
After introducing Na ₂ SiF ₆ , days:											
1	73.30	26.02	0.062	0.40	—	—	15.21	86.8	0.016	37.5	0.041
20	73.51	25.72	0.064	0.35	1460	1150	18.27	87.0	0.016	40.0	0.058
30	73.44	25.79	0.061	0.34	—	—	18.27	86.2	0.021	48.8	0.580
85	73.50	25.83	0.061	0.46	—	—	18.22	86.2	0.021	48.8	0.580
95	73.15	25.80	0.065	0.42	—	—	18.28	84.5	0.025	54.3	0.580
240	73.73	25.57	0.066	0.38	—	—	19.30	86.2	0.020	43.3	0.580

The chemical composition of glasses produced before and after the introduction of the melting catalyst Na₂SiF₆ (TU 113-08-587-86) and the technological parameters of the process are given in Table 1. The catalyst was introduced under conditions of continuous production. Before Na₂SiF₆ was introduced, a constant content of the basic glass components satisfying the composition prescribed by regulatory documents was observed. Introduction of the catalyst fostered a decreased melt viscosity and, accordingly, decreased temperatures of clarification and molding, which agrees well with the data in [1, 5]. The crystallization parameters of the glass changed insignificantly here. The Fe₂O₃ content (found from analysis) before and after the modification of the technology was within the limits of 0.057 – 0.066%.

At the same time (for a stable technological process), a decrease in the integral light transmission per cm of glass thickness from 86.7% in the initial glass to a minimum value of 84.5% (on adding 0.58% accelerator) was recorded. It was found that this effect was due to an increase in the content of iron in the lower degree of valence from 0.016 – 0.017% on the average (without the catalyst) to 0.021% (after introducing Na₂SiF₆). In certain periods the content of reduced iron reached 0.25% and exceeded the same parameter in glasses without Na₂SiF₆ by 64 – 68%.

In order to maintain the optimum level of glass-melt diathermancy, the ratio of sodium sulfate and anthracite in the batch was adjusted, as a consequence of which the batch ROP increased from 15.06 (without the catalyst) to 19.30 (with the catalyst). The batch ROP was calculated in accordance with the recommendations given in [1].

Use of the glass basicity index makes it possible to describe in detail the dynamics of the change in the glass-melt ROP upon introduction of the melting catalyst.

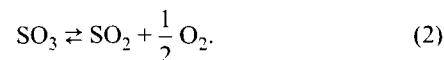
In the initial state, the reduced-iron fraction $d_{\text{Fe(II)}}$ was equal to 37.9%. Introduction of 0.41% Na₂SiF₆ into the batch, all else being equal, did not change the degree of iron oxidation, which indicates the inefficiency of small quanti-

ties of Na₂SiF₆ additive. Subsequently, on increase in the accelerator content in the batch to 0.58%, the bivalent-iron fraction started growing, which caused decreased diathermancy of the glass melt.

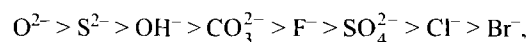
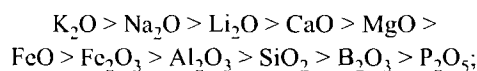
The introduction of Na₂SiF₆ generated two processes that have opposite effects with respect to the melting rate: on the one hand, it decreased the melt viscosity and, accordingly, increased the rate of glass melting and clarification, and on the other hand, it decreased the diathermancy of the melt, overheated the upper layers, and, possibly, overcooled the deep layers, which ultimately compensated for the acceleration caused by the decreased viscosity. Moreover, the large temperature gradient across the glass-melt depth resulted in increased heat radiation from the upper layer into the furnace flame space, which led to accelerated roof wear.

In order to avoid the negative consequences of decreased diathermancy for glass melting, the batch ROP was increased to 18.26 and even to 19.30.

It is noteworthy that the SO₃ content in the glass decreased from 0.50 ± 0.03 to 0.38 ± 0.03%. In our opinion, this is a consequence of the change in the glass-melt ROP related to the change in the redox equilibrium of sulfur [1] present in the melt:



Introduction of sodium silicofluoride probably leads to increased acidity of the glass melt due to formation of the fluoride ion F⁻. Taking into consideration the two series of elements with increasing acidity [7, 8]



in conformity with the Le Chatelier principle an increase in the melt acidity should shift the equilibrium toward forma-

tion of elements with a lower acidity. In our case, this is exactly what happens. Similarly to the above case with iron, the redox equilibrium (2) is partially shifted to formation of sulfur with a lower degree of oxidation and atomic oxygen. Moreover, unlike SO_3 , which is readily soluble in the glass melt and is a surfactant [1], SO_2 is virtually insoluble in silicate melts and is released from the melt into the gas space of the furnace together with the oxygen formed by reaction (2). In this way, the content of the acid ion SO_4^{2-} decreases due to the external increase in acidity caused by the introduction of sodium silicofluoride, which maintains the acid-base equilibrium of the melt.

The emission of gaseous components from the melt is intensified probably, due to the continuing dissociation reaction of residual sodium silicofluoride [1] with formation of silicon fluoride. Under conditions of decreased viscosity, the gaseous sulfur, fluorine, and oxygen compounds leaving the melt activate the glass-melt clarification process in the furnace.

Thus, in response to the external action, i.e., introduction of sodium silicofluoride, which increases the melt acidity, the equilibrium of the system, characterized by vapors of oxides of variable valence



shifts toward formation of more reduced elemental forms, which decreases the melt ROP to the equilibrium value for the given temperature and composition of the gaseous phase above the melt. All this results in decreased diathermancy of the glass melt due to the increased amount of bivalent iron,

and therefore, along with introduction of sodium silicofluoride, the batch ROP should be adjusted toward greater oxidizing capacity.

In spite of the fact that the use of Na_2SiF_6 in glass technology is restricted due to environmental considerations, the data obtained permit a more profound understanding of its effect on the redox potential of the glass melt.

REFERENCES

1. H. Bach, G. K. Baukke, G. Bruckner, et al. (eds.), *Types of Defects in Glass Production* [in Russian], Stroiizdat, Moscow (1986).
2. Yu. A. Guloyan, *Efficiency of Technological Processes in Production of Glass Articles* [in Russian], Legkaya i Pishchevaya Prom-st', Moscow (1982).
3. V. A. Barachevskii, G. I. Lashkov, and V. A. Tsekhomskii, *Photochromy and Its Applications* [in Russian], Khimiya, Moscow (1977).
4. S. P. Antonova, "The effect of accelerating additives for glass melting on spectral characteristics of tinted light filters," *Steklo Keram.*, No. 10, 14 – 15 (1987).
5. R. S. Zolotareva, N. I. Min'ko, V. A. Obrezan, et al. "On the effect of sodium silicofluoride in high-temperature melting of technical glass," *Steklo Keram.*, No. 7, 7 – 10 (1976).
6. É. K. Polokhlivets, V. I. Kiyan, and A. B. Atkarskaya, "Change in the glass composition in an operating furnace," *Steklo Keram.*, No. 11, 12 – 15 (1998).
7. D. S. Korzhinskii, "Acid-base interaction of the components in silicate melts and the direction of isothermic lines," *Dokl. Akad. Nauk SSSR*, **128**(2), 383 – 386 (1959).
8. D. N. Kocharko, "The principle of chemical-bond polarity and its significance in the geochemistry of magnetism," *Geokhimiya*, No. 9, 1286 – 1297 (1980).